

Lead Sulphide Colloidal Quantum Dots for Sensing Applications

A. De Iacovo, C. Venettacci, S. A. Bruno and L. Colace
Department of Engineering, University Roma Tre, Via Vito Volterra 62, Rome, Italy

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Abstract: Colloidal Quantum Dots (CQD) have been widely studied for their peculiar optical characteristics such as enhanced optical absorption and tunable absorption spectrum. Many different photodetectors have been proposed but overall performance is still poor from the point of view of the bandwidth and noise performance. Here we propose the employment of a PbS QD photoconductor as an ultra-high sensitivity fire detector, exploiting the outstanding device responsivity at low optical powers. Moreover, we demonstrate the outstanding flexibility of CQD based devices, employing our detectors also as simple pollution gas sensors for NO₂ detection.

1 INTRODUCTION

Colloidal Quantum Dots (CQD) are semiconductor nanoparticles directly synthesized and dispersed in solution. The synthesis process is straightforward and does not require high vacuum or high temperature (Pu et al. 2018). Moreover, the final material characteristics can be easily tailored through the modification of simple parameters such as reaction time and temperature. Being nano-sized, the quantum dots show peculiar optical, electronic and chemical characteristics such as enhanced optical absorption and resonant absorption spectra (Moreels et al. 2009), ease of doping (even after material synthesis and directly on the deposition substrate) (Kagan et al. 2016) and outstanding reactivity with several chemical species thanks to the high surface-to-volume ratio. Being dependent on the nanoparticle size, all these characteristics can be easily tailored during the QD synthesis, leading to a variety of similar colloidal materials with a vast range of physical properties.

Thanks to their characteristics, colloidal quantum dots have been employed for the realization of several different kind of devices, such as photodetectors (De Iacovo et al. 2016), solar cells (Sargent 2012), light emitting diodes (Caruge et al. 2008) and chemoresistors (Liu et al. 2014). In general, all these devices exploit the ease of formation of QD films and either their outstanding optical properties or their very high surface-to-volume ratio and chemical reactivity.

Among several different materials in the class of CQDs, lead sulphide (PbS) has been widely employed for the fabrication of near-infrared photodetectors; its absorption edge can easily be tuned, by quantum-confinement effect, from 900nm to 1.8 μ m (Moreels et al. 2009) and its synthesis route is well established, producing colloids that are stable over a long period of time. The as-synthesized colloid is usually stabilized with an organic, long-chained capping agent such as oleic acid. Such colloids can be readily deposited on a variety of substrates to produce QD films; in this case, however, the nanoparticles in the solid film are arranged with a mean distance twice as long as the molecular chain of the capping agent. Such a distance is, typically, too long for the film to be conductive because charges cannot easily tunnel from one dot to another. To enhance the film conductivity, a ligand exchange procedure is usually necessary. The long-chained ligands are stripped away from the QD surface (either in solution or directly from the deposited film) and substituted with shorter ones, thus enabling charge transfer between neighbouring nanocrystals.

This approach can be carried out on a variety of substrates, comprising silicon and SiO₂. PbS QDs have been employed for the realization of photodetectors and transistors directly on silicon substrates, thus enabling their integration with silicon electronics in a more-than-Moore framework (Balazs et al. 2014). Nevertheless, the resulting devices still show poor performance in terms of noise and bandwidth and the technology is not yet comparable

to other well-established more-than-Moore approaches such as Ge-on-Si (Soriano et al. 2010) (Soriano et al., 2015). Poor device performance can usually be attributed to very low electron mobility and high noise which, in turn, limit the device bandwidth and detectivity (De Iacovo et al. 2017). For these reasons, CQD based devices are more suitable for sensing applications, where high sensitivity and low bandwidth are required.

In this paper we show our recent work with PbS QD devices for sensing applications both in the optoelectronic and gas sensing field. In particular, we propose a high-gain, visible-blind, photoconducting photodetector for indoor flame detection and a chemoresistive gas sensor for NO₂.

2 DEVICE FABRICATION

The devices have been fabricated employing a commercial 10mg/mL PbS QD solution in toluene with mean particle diameter of 5nm (Sigma-Aldrich). This particular type of nanoparticle has a first excitonic absorption peak located near 1360nm. The nanoparticles are capped with oleic acid and the first fabrication step consists in the removal of the long-chained ligand by centrifugation in excess methanol. The precipitated nanocrystals are then washed with methanol and any residual solvent is evaporated in a vacuum desiccator. The QDs are redispersed in octane with a 0.8mg/mL final concentration. The new QD solution is drop casted on a SiO₂ substrate with pre-patterned gold interdigitated contacts and the devices are kept in a desiccator until full solvent evaporation. Butylamine is then drop-casted onto the QD film. In this step the amine ligates to the nanocrystal surface and the QDs in the film are rearranged with a short mean distance (0.6nm) corresponding to the length of the organic molecule. QD and butylamine drop-casting are repeated 10 times to create a nanocrystal film with a mean thickness of 1 μ m. Eventually, the devices are rinsed with methanol for 2 hours to remove all the butylamine and improve QD packing (Konstantatos et al., 2006). For the fabrication of the visible-blind photodetectors, the devices are enclosed in a packaging with a silicon optical window that acts as a filter for visible wavelengths. Conversely, devices meant as gas sensors are readily usable after fabrication.

3 VISIBLE-BLIND PHOTODETECTORS AND FLAME SENSORS

The photodetectors were initially characterized in terms of current-voltage characteristics to verify the device resistivity and the ohmicity of the Au-QD contact. Fig. 1 shows the resistance of three different devices with interdigitated finger spacings ranging from 5 to 20 μ m. As expected, the resistance increases with the finger spacing. The devices show a linear I-V characteristic (Fig. 1, inset) confirming the ohmicity of the Au-QD contact.

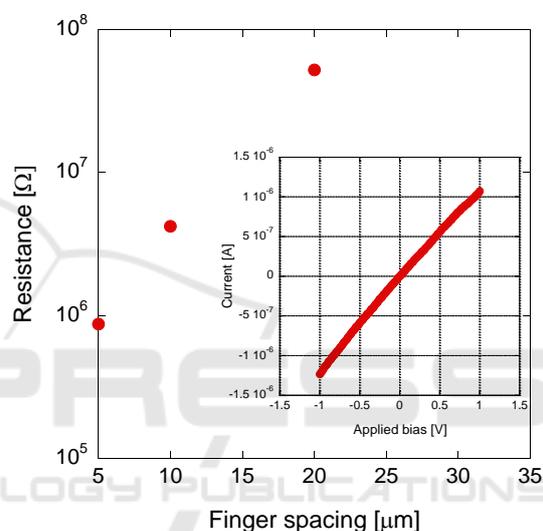


Figure 1: Device resistivity vs. interdigitated finger spacing. Inset: voltage-current characteristics of a 5 μ m device.

A semiconductor laser at 1300nm has been employed for the characterization of the device's photoresponse. Fig. 2 shows the measured responsivity and its dependence on the applied bias. As expected for a photoconductor, responsivity is proportional to the applied bias and at 1V it is higher than 1A/W. Thus, the photodetector shows a photoconductive gain. This phenomenon has been previously observed in similar devices and should be attributed to the long electron lifetime due to the presence of deep electron traps with a reduced cross-section for holes (Konstantatos et al. 2007). The presence of such a trapping mechanism usually induces a nonlinear response in the photodetector. At low incident optical power, in fact, all the photo-generated electrons can be trapped and the photoconductive gain is maximum; conversely, when the photo-generated carriers outnumber the available

trap states, some electron can be swept throughout the device and can be collected at the gold contacts in a time much shorter than the mean electron lifetime. In this case the overall photoconductive gain is reduced. In order to verify this behavior, we characterized the device varying the incident optical power. Fig. 3 shows the obtained R vs. P characteristics. As

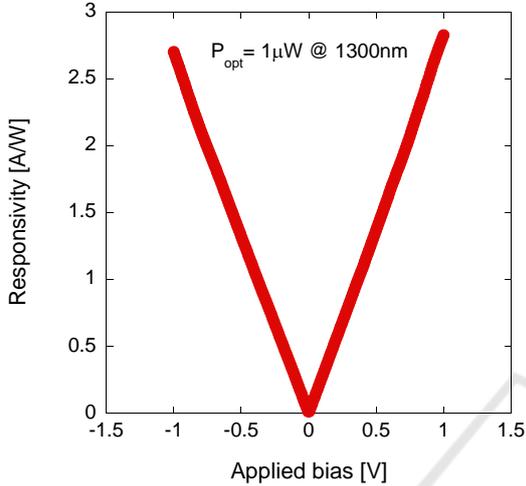


Figure 2: Responsivity vs. voltage characteristics of a 5µm photodetector.

expected, the responsivity has a strong dependence on the optical power and reaches a plateau around 5nW. It should be observed that, given the low operating voltage, our devices show a responsivity performance comparable with state-of-the-art PbS QD photoconductors (Saran et al. 2016).

The high responsivity at low incident optical power can be exploited for the realization of detectors for fire and flame sensing applications. It is well known that a hot body emits an optical radiation whose spectrum is described by Planck's law as defined in (1), where B is the spectral irradiance at the optical frequency ν and temperature T , h is the Planck constant, K is the Boltzmann constant and c is the speed of light.

$$B(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{KT}} - 1} \quad (1)$$

A flame, burning between 900 and 1100°C (Babrauskas 1980), emits a radiation with a wide spectrum from the visible wavelengths to the infrared, peaked at around 1800nm. Being highly sensitive in the NIR region of the spectrum, the PbS CQD photoconductor can be easily employed for flame detection but, in order to avoid false detection due to ambient illumination, a visible light filter must be included. As previously mentioned, we encapsulated

the photodetector in a packaging provided with a silicon window which completely absorbs radiation in the visible range. Fig. 4 shows both the spectral responses of the unpackaged (red curve) and packaged (blue curve) photodetector. The silicon filter absorbs all the light below 900nm. Fig. 4 also shows the presence of the excitonic absorption peak of the PbS QDs at 1360nm.

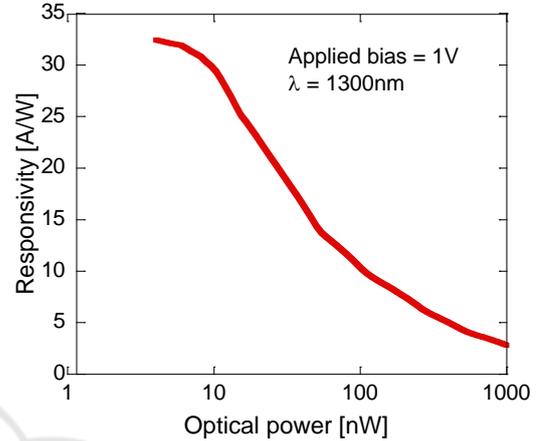


Figure 3: Responsivity vs. incident optical power.

The removal of any radiation with $\lambda < 900\text{nm}$ implies that the device can be effectively employed for flame detection in an indoor environment. Light sources used in domestic environment, in fact, don't emit any infrared radiation that could interfere with flame detection. Conversely, sunlight could prevent the detector's operation. We tested our device in a closed room with standard office illumination (neon lamps, 250 lm/m²) lighting a wax candle in front of the photodetector and varying the distance between the candle and the detector surface. Fig. 5 shows the percent variation of the measured current with respect to the dark current at 1V bias; as expected, photocurrent follows an inverse square law with the flame distance.

We also measured the mean dark current and its standard deviation over 10 minutes, obtaining $\sigma = 0.25\%$. We defined a flame detection threshold that is 20 times larger than σ (5%). This threshold and its intercept with the detection curve are represented with dashed lines in Fig. 5. The detection threshold is reached when the candle is lit 17.9m from the detector's surface.

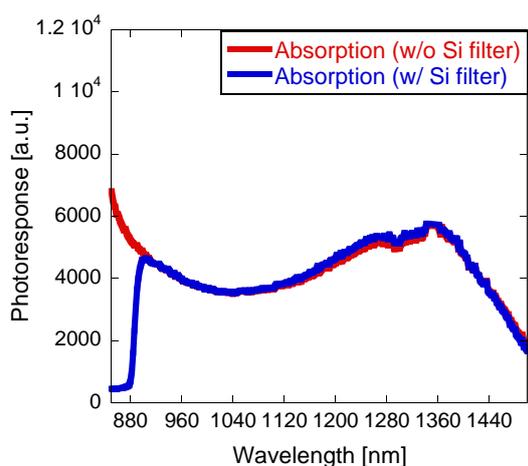


Figure 4: Spectral response of the PbS CQD photodetector with (blue curve) and without (red curve) the silicon filter.

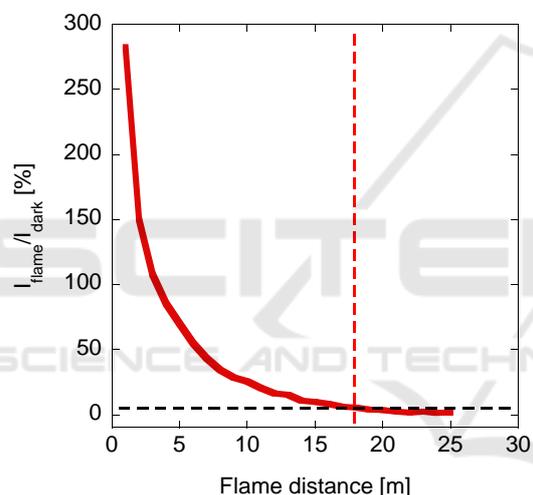


Figure 5: Detector current variation vs. candle flame distance.

Given the device resistance and the applied voltage, we also evaluated the mean power dissipation of the flame detector as $P_{diss} = V^2/R \approx 1.2 \mu W$.

Eventually, we verified that the detector response was not modified with respect to environment illumination. We tested our device from complete dark to strong indoor illumination (neon and LED lamps, 1000-2000 lm/m^2) and could not observe any difference in the detector behavior.

Our results demonstrate that a PbS QD photodetector can be effectively employed as a high-sensitivity flame detector for indoor safety systems, providing very high detection distance and low power consumption.

4 POLLUTION GAS SENSOR

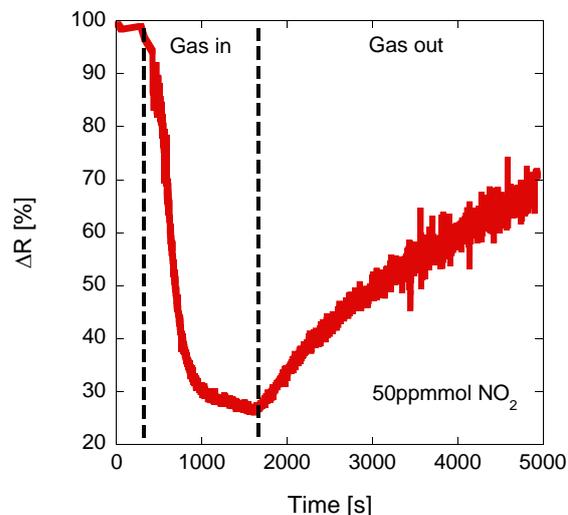


Figure 6: PbS QD sensor resistance variation in response to 50ppmmol NO_2 .

QD surface chemistry plays a key role in the determination of the electronic characteristics of CQD electron devices (Brown et al., 2014); oxidation of the QD film, in particular, has shown dramatic effects on the performance of PbS photodetectors (De Iacovo et al., 2016). One of the main class of polluting gases is represented by nitrous oxides (NO_x) and we tested our devices as gas sensors for NO_2 detection. The devices were wire bonded to a custom chip carrier and inserted into an enclosed test chamber where we fluxed pure nitrogen and NO_2 , varying the proportional flux of the pollutant gas. Fig. 6 shows the typical resistance variation of a PbS QD resistor (finger spacing = $20 \mu m$) in response to 50ppmmol of NO_2 . The sensor shows a slow response to the gas, reaching a resistance plateau after 10 minutes of fluxing. Also, gas desorption is very slow and complete recovery happens only after 1.5 hours. We evaluated the sensor response to different gas concentrations. Fig. 7 shows the percent resistance variation with respect to the ppm of NO_2 fluxed into the measurement chamber and the corresponding linear fit. We evaluated a resistance variation of 1.5%/ppm corresponding to $3 M\Omega/ppm$.

Our results are promising for future development of PbS CQD based sensors for pollutant gas detection, nevertheless, the slow response and recovery time are still an issue. A possible approach to enhance device response and recovery time should consist in a reduction of the thickness of the QD film.

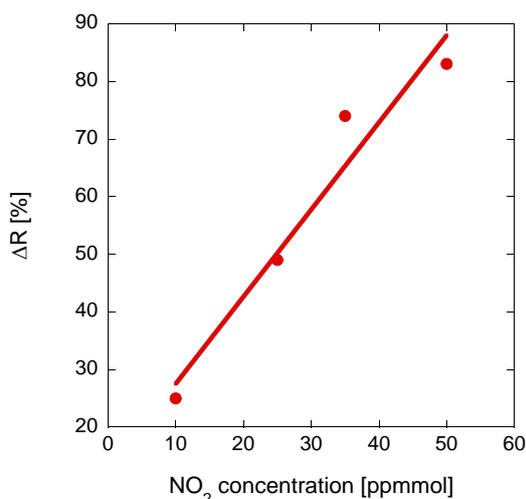


Figure 7: Device resistance variation for different NO₂ concentrations. Experimental data (points) and linear fit (line).

We determined the sensor noise by continuously measuring its resistance with no gas flow for 10 minutes and determining the standard deviation of the acquired data. We employed this data to extrapolate the theoretical detection limit of our sensor obtaining a minimum detectable NO₂ concentration of 4.9ppb. Even if our detector shows lower performance if compared to other PbS QD based NO₂ sensors (Song et al., 2018), it should be noted that we propose a device that is already integrated on a Si/SiO₂ substrate and that, consequently, could be easily coupled with readout electronics to produce a standalone NO₂ gas sensor with a more-than-Moore approach. Moreover, device parameters such as QD film thickness and metal finger spacing could be optimized to enhance the device response. This analysis is, however, out of the scope of this paper and will be discussed in future publications.

5 CONCLUSIONS

In this paper we showed our results with optical and chemical sensors based on PbS colloidal quantum dots. We showed how the same CQD device, with only slight modifications in the fabrication process, can have manifold applications for different sensing purposes. We proposed a novel fire detector with ultra-high sensitivity for indoor applications and a pollution gas sensor integrated on a Si/SiO₂ substrate, defining a strategy for future sensor integration with silicon electronics.

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